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Synthesis and characterisation of alkyl-*N*,*N'*-bis(salicylidene)-ethylenediamino- and alkyl-*N*,*N'*-bis(salicylidene)-1,2-phenylenediaminogallium or indium complexes: crystal structure of methyl-*N*,*N'*-bis(salicylidene)-1,2-phenylenediaminoindium

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Abstract

The reaction of trialkylgallium or indium R_3M (M = In, Ga; R = Me, Et) with *N*,*N'*-ethylenebis(salicylideneimine) or 1,2-*N*,*N'*-phenylenebis(salicylideneimine) yields seven intramolecularly coordinated organogallium or organoindium complexes. Two hydroxyl protons in the ligands react with both trialkylindium and trimethylgallium, while one hydroxyl group reacts exclusively with triethylgallium. The complexes obtained have been fully characterised by elemental analysis, ^{1}H-NMR, IR and mass spectroscopy. The structure of methyl-*N*,*N'*-bis(salicylidene)-1,2-phenylenediaminoindium (**1**) has been determined by single-crystal X-ray analysis. The In atom is five coordinate in the structure. Fluorescence spectroscopy has shown that the maximum emission wavelength of **1** is 499 nm upon radiation by UV light. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Trialkylgallium; Trialkylindium; Organometallic complex; Schiff base; Luminescent

1. Introduction

Organoaluminium, gallium and indium complexes, which contain either Group 15 or 16 elements, have been under investigation for many years due to their rich structural information and wide applications in material science [1–3] and organic reactions [4,5]. Organic electroluminescent (OEL) devices have recently received much attention because of their potential emission of all colours (from blue to red) and their possible applications in large-area light displays [4–6]. Tris(8-hydroxyquinoline)aluminium (Alq_3) [7] is one of the typical examples of an OEL emitting material. Although there are many reports on OEL devices in recent years [8], the application of organoaluminium, gallium or indium complexes as OEL materials has been rarely studied [9]. Application of Group 13 organometallic compounds in OEL materials will certainly create a new variety in this field. The structures of salicylaldehyde Schiff bases are similar to that of 8-hydroxyquinoline, in that they both have at least one hydroxyl group, a coordination nitrogen atom, and a delocalised π-system; however, the structures of salicylaldehyde Schiff bases are certainly more flexible than that of 8-hydroxyquinoline. Organometallic complexes of salicylaldehyde Schiff base ligands are expected to show good luminescent properties. As part of our efforts in searching for new OEL substances, we wish to report here the synthesis and characterisation of alkylgallium and indium complexes LMR (H_2L = *N*,*N'*-ethylenebis(salicylideneimine) or 1,2-*N*,*N'*-phenylenebis(salicylideneimine), R = CH_3, M = Ga, In; R = Et, M = In) and $(HL)GaEt_2$. The

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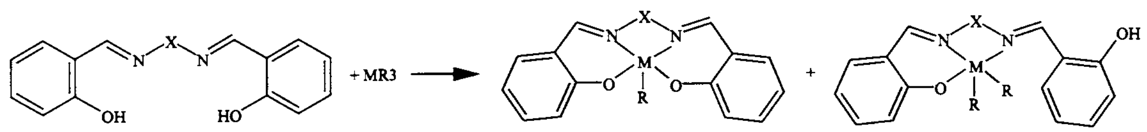

1-5 **6,7**

	M	R	X		M	R	X
1	In	Me	C_6H_4	**5**	Ga	Me	CH_2CH_2
2	In	Et	CH_2CH_2	**6**	Ga	Et	C_6H_4
3	In	Et	C_6H_4	**7**	Ga	Et	CH_2CH_2
4	Ga	Me	C_6H_4				

Scheme 1.

crystal structure of methyl-*N*,*N*′-bis(salicylidene)-1,2-phenylenediaminoindium (**1**) has been determined by X-ray analysis and the luminescent emission spectrum of **1** has also been measured.

2. Results and discussion

The reaction of gallium and indium alkyls R_3M (M = Ga, In; R = Me, Et) with the Schiff base ligands, *N*,*N*′-ethylenebis(salicylideneimine) and 1,2-*N*,*N*′-phenylenebis(salicylideneimine), proceeded smoothly at room temperature in a 1:1 ratio affording the corresponding intramolecularly coordinated complexes as shown in Scheme 1. The complexes were isolated as yellow solids in high yields. Although gallium and indium alkyls are extremely moisture and oxygen sensitive, the complexes obtained are fairly stable on exposure to air. Compounds **1**–**5** could be left in an ambient atmosphere for weeks without obvious decomposition. The complexes are insoluble in cold saturated hydrocarbons, such as pentane or petroleum, whereas they are highly soluble in unsaturated hydrocarbons, such as benzene or toluene. All the products obtained gave satisfactory elemental analysis results, and were characterised by IR, ^{1}H-NMR and MS spectroscopy.

Two active hydroxyl protons in the ligands of *N*,*N*′-ethylenebis(salicylideneimine) and 1,2-*N*,*N*′-phenylenebis(salicylideneimine) reacted with trimethylgallium, trimethylindium and triethylindium to form the monoalkyl complexes **1**–**5** with methane or ethane eliminated as by-products. In both the IR and ^{1}H-NMR spectra of the complexes, there were no O–H signals. By comparison with the IR spectra of the free ligands, the C–H stretch vibration band of the complexes were relatively stronger. In the ^{1}H-NMR spectra, the signals due to the metal-bonded methyl or methylene signals were found to shift downfield from those of the metallic trialkyls. Reactions of triethylgallium with the ligands, however, formed predominantly the diethylgallium products (**6** and **7**), possibly due to the steric effects around the metal centre. The radius of gallium is smaller than that of indium and an ethyl group is also sterically bulkier than a methyl group. Once one ethyl group is eliminated from the gallium, the crowded gallium centre may prevent the second hydroxyl group from approaching. The structure was confirmed by IR and ^{1}H-NMR spectroscopy. The signals of OH protons in the spectra were visible. In their ^{1}H-NMR spectra, the O–H signals were observed at 12.76 and 12.83 ppm for **6** and **7**, respectively. In the IR spectra of **6** and **7**, the strong O–H absorption appeared at 3454 and 3495 cm^{-1}, respectively. The molecular ion peaks of complexes **1**, **4** and **5** were observed in MS spectra, suggesting that the complexes are fairly stable, even in the ionic state. Although there were no M^+ peaks for other complexes, fairly intensive fragments were observed upon elimination of one or two alkyls. The relative intensity of the peaks for the metal containing species agreed well with the isotopic distribution of the metals (^{69}Ga (ca. 60%); ^{71}Ga (ca. 40%) and ^{113}In (ca. 9%); ^{115}In (ca. 91%)).

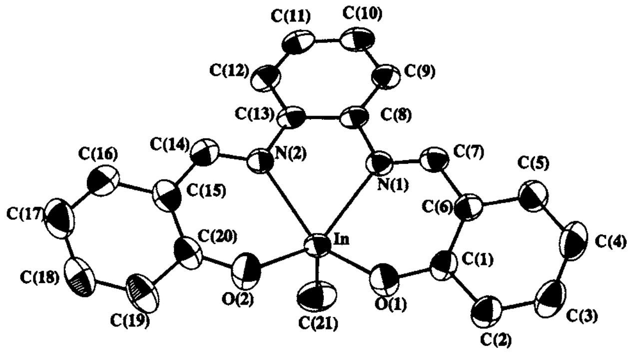

Fig. 1. Molecular structure of methyl-*N*,*N*′-bis(salicylidene)-1,2-phenylenediaminoindium (**1**) showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for $C_{21}H_{17}N_2O_2In$ (**1**)

Bond lengths			
In–O(1)	2.092(4)	In–O(2)	2.093(4)
In–N(1)	2.258(4)	In–N(2)	2.265(4)
In–C(21)	2.133(7)	O(1)–C(1)	1.313(6)
O(2)–C(20)	1.301(7)	N(1)–C(7)	1.283(6)
N(1)–C(8)	1.401(6)	N(2)–C(13)	1.397(6)
C(6)–C(7)	1.437(6)	C(8)–C(13)	1.421(7)
C(15)–C(20)	1.416(8)	C(1)–C(6)	1.417(7)
Bond angles			
O(1)–In–O(2)	90.7(2)	O(1)–In–C(21)	110.9(2)
O(1)–In–N(1)	83.8(2)	C(1)–C(6)–C(7)	125.1(4)
O(1)–In–N(2)	138.3(2)	O(2)–In–C(21)	113.0(3)
O(2)–In–N(1)	133.0(2)	O(2)–In–N(2)	82.8(2)
C(21)–In–N(1)	112.4(2)	C(21)–In–N(2)	109.5(2)
N(1)–In–N(2)	71.6(1)	C(1)–O(1)–In	130.0(3)
C(20)–O(2)–In	131.1(4)	C(7)–N(1)–In	125.8(3)
C(8)–N(1)–In	112.7(3)	C(14)–N(2)–In	127.0(4)
C(13)–N(2)–In	111.8(3)	N(1)–C(7)–C(6)	126.7(4)
N(1)–C(8)–C(13)	116.0(4)	C(7)–N(1)–C(8)	121.4(4)
N(2)–C(13)–C(8)	115.8(4)	N(2)–C(14)–C(15)	125.7(5)
C(14)–N(2)–C(13)	121.2(4)	C(20)–C(15)–C(14)	124.4(4)
O(1)–C(1)–C(6)	124.0(4)	O(2)–C(20)–C(15)	125.3(5)
O(2)–C(20)–C(19)	117.6(5)		

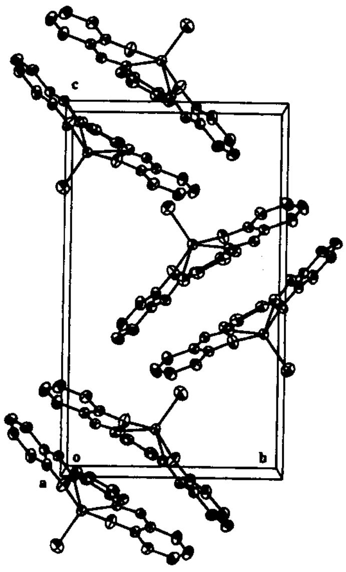

Fig. 2. Structure unit cell of **1**.

The structure of complex **1** was determined by single-crystal X-ray analysis. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. In the structure, the In atom is in a distorted quadra-pyramidal configuration with the formation of three new indium rings involved. The In atom is five-coordinately bonded to two nitrogen atoms and one oxygen atom. The three phenyl rings bridged by the two imine linkages are, as expected, almost in the same plane, indicating that the three phenyl rings are well conjugated. The In–C(21) bond is approximately perpendicular to the plane. The In–O distances (2.092(4) Å for In–O(1) and 2.093(4) Å for In–O(2)) are shorter than those reported for dimethyl[μ-(2-pyridinecarboxaldehydeoximato)]indium (2.241(16) and 2.229 (14) Å) [10] and dimethyl(salicylaldehyde)indium (2.188(3) Å) [11]. This suggests that In–O bonding in compound **1** is very strong. The In–N distances in **1** (2.258(4) and 2.265(4) Å for In–N(1) and In–N(2), respectively) are also shorter than those in Me_3In-$NHMe(CH_2)_2NHMeInMe_3$ (2.369(7) and 2.393(7) Å) and $Me_3InNHCMe_2(CH_2)_3CMe_2$ (2.502(5) Å). This means that the In–O–O–N–N pyramidal structure is rigid in the complex. It is very interesting to note that every two molecules of the complex are situated face-to-face in the solid state, as shown in the unit cell (Fig. 2). The two molecules are just like two gongs folded closely, suggesting that there are some electronic interactions between the two molecules, at least in the solid state. There is also a weak intermolecular CH/π interaction between the indium-bonded methyl group of one molecular and the C(1A)–C(2A)–C(3A)–C(4A)–C(5A)–C(6A) ring of the other [16]. The nearest distance (H(16)–C(5A)) is 3.18 Å.

An emission spectrum of complex **1** in chloroform showed that **1** fluoresces in the blue–green region (see Fig. 3). The emission maximum was at $\lambda = 499$ nm with an intensity of 53 cd m^{-2}. The intense emission band suggests that the incorporation of the organoindium group to the ligand increases its emission efficiency. Fluorescence properties of other compounds and their OEL properties are now under investigation by our group.

3. Experimental

All reactions were performed in a glove box under purified nitrogen. The solvents were refluxed with sodium benzophenone and distilled under nitrogen prior to use. The Schiff-base ligands were prepared by condensation of salicylaldehyde with ethylenediamine or 1,2-phenylenediamine. Trimethylgallium, triethylgallium, trimethylindium and triethylindium were pro-

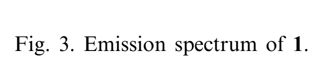

Fig. 3. Emission spectrum of **1**.

vided by the National 863 Program Advanced Material MO Precursors R&D Center of China. ^{1}H-NMR data were collected on Bruker AM-500 and Jeol PMX-60SI spectrometers with TMS as the internal standard (solvent: C_6D_6). IR spectra were obtained as KBr pellets on a 5DX-FT-2 spectrometer. Mass spectra was measured on a VG-ZAB-HS spectrometer (electron impact ionisation). Luminescent spectra were measured on a RF-5000 fluorimeter. Elemental analyses were performed on a Perkin–Elmer 240C elemental analyser. Melting points were observed in sealed capillaries and were uncorrected.

*3.1. Synthesis of methyl-N,N′-bis(salicylidene)-1,2-phenylenediaminoindium (**1**)*

To a solution of 1,2-*N*,*N*′-phenylenebis(salicylideneimine) (0.632 g, 2 mmol) in 10 ml cyclohexane was added dropwise a solution of triethylindium (0.32 g, 2 mmol) in 10 ml benzene over a period of 10 min with stirring. On addition of trimethylgallium, methane gas was evolved immediately from the mixture. Then the mixture was stirred for an additional 5 min at room temperature (r.t.). The volatiles were removed under vacuum and the yellow powder residue was recrystallised from a cyclohexane–benzene mixture. Compound **1** was obtained as yellow crystals. Yield: 82.3%; m.p. 263–264°C. IR (cm^{-1}): 3072 (w), 3007 (w), 2917 (w), 1609 (vs), 1581 (m), 1525 (m), 1461 (m), 1391 (m), 1328 (m), 1180 (w), 1152 (w), 920 (w), 752 (w), 533 (w). ^{1}H-NMR (ppm, in C_6D_6): 8.45 (s, 2H, $-CH=$N), 6.5–7.5 (m, 12H, *Ar–H*), − 0.03 (s, 3H, InCH_3). MS: 445 (2.2%), 444 (9.86%), 429 (92.64%), 327 (2.88%), 115 (100%), 78 (22.58%). Anal. Calc. for $C_{21}H_{17}N_2O_2In$: C, 56.78; H, 3.86; N, 6.31. Found: C, 56.74; H, 3.81; N, 6.36%.

*3.2. Synthesis of ethyl-N,N′-bis(salicylidene)-1,2-phenylenediaminoindium (**2**)*

Compound **2** was prepared and purified in a manner similar to that described for **1** from 1,2-*N*,*N*-phenylenebis(salicylideneimine) (0.623 g, 2 mmol) and triethylindium (0.404 g, 2 mmol). The compound was isolated as yellow crystals. Yield: 0.74 g (81.2%); m.p. > 210°C. IR (cm^{-1}): 3054 (w), 2956.4 (w), 2937 (w), 2906 (w), 2858 (w), 1608 (vs), 1584 (s), 1533 (vs), 1462 (s), 1444 (s), 1387 (s), 1347 (w), 1313 (s), 1252 (w), 1181 (s), 1150 (s), 1125.6 (w), 1032.8 (w), 919.9 (w), 848 (w), 799.8 (w), 754 (s), 686.5 (m), 530.2 (m). ^{1}H-NMR (ppm, in C_6D_6): 8.53 (s, 2H, $-CH=$N), 6.60–8.0 (m, 12H, *Ar–H*), 1.02 (t, 3H, GaCH_2CH_3), 0.75 (q, 2H, InCH_2CH$_3$). MS: 316.9 (9.30%), 216.9 (30.49%), 214.9 (12.52%), 213.0 (11.65%), 108.9 (33.03%), 91.0 (100.00%), 89.9 (11.21%), 72.9 (27.72%), 61.0 (14.41%), 57.0 (25.93%). Anal. Calc. for $C_{22}H_{19}N_2O_2In$: C, 57.66; H, 4.18; N, 6.12. Found: C, 57.80; H, 4.33; N, 6.24%.

*3.3. Synthesis of ethyl-N,N′-bis(salicylidene)ethylenediaminoindium (**3**)*

Compound **3** was prepared in a manner similar to that described for **1** from *N*,*N*′-ethylenebis(salicylideneimine) (0.536 g, 2 mmol) in 10 ml and 2 ml benzene and triethylindium (0.41 g, 2.0 mmol) in cyclohexane–benzene mixture. The yellow crystal of **2** was isolated. Yield: 0.71 g (86.5%); m.p. 227–228°C. IR (cm^{-1}): 3046.6 (w), 3020 (w), 2952 (w), 2935 (w), 2907 (w), 2895.4 (w), 1646.8 (vs), 1628.3 (vs), 1598.9 (m), 1537 (s), 1465.8 (s), 1444.8 (m), 1392.4 (w), 1335.4 (m), 1305 (m), 1198.6 (m), 1149.4 (m), 1048.4 (w), 906 (w), 758.1 (vs), 643 (w), 607.4 (w). ^{1}H-NMR (ppm, in C_6D_6): 8.10 (s, 2H, $-CH=$N), 6.53–7.27 (m, 8H, Ar–*H*), 3.76 (m, 4H, –N(CH_2)$_2$N–), 1.05 (t, 3H, InCH$_2CH_3$), 0.77 (q, 2H, InCH_2CH$_3$). MS: 383 (9.59%), 381 (1.69%), 269.3 (30.78%), 267.3 (4.27%), 251.1 (7.20%), 177.2 (17.48%), 165.2 (8.61%), 148.2 (23.8%), 134.2 (8.89%), 133.2 (9.19%), 122.1 (10.00%), 121.1 (12.51%), 120.1 (12.66%), 116.3 (100.00%), 107.2 (15.83%), 77.1 (10.22%), 73.1 (18.56%), 59.0 (16.26%), 57.1 (10.27%). Anal. Calc. for $C_{18}H_{19}N_2O_2In$: C, 52.68; H, 4.67; N, 6.83. Found: C, 52.67; H, 4.75; N, 6.90%.

*3.4. Synthesis of methyl-N,N′-bis(salicylidene)-1,2-phenylenediaminogallium (**4**)*

A solution of trimethylgallium (0.23 g, 2 mmol) in 10 ml cyclohexane was added dropwise over a period of 10 min with stirring to a solution of 1,2-*N*,*N*′-phenylenebis(salicylideneimine) (0.632 g, 2 mmol) in a mixture of 10 ml cyclohexane and 2 ml benzene. After the mixture was stirred for an additional 5 min at r.t., the solvent was removed under vacuum and the yellow powder residue was recrystallised from a cyclohexane–benzene solution, giving pale yellow crystals of **4**. Yield: 0.658 g (82.4%); m.p. 110–111°C. IR (cm^{-1}): 3057.8 (w), 3022 (w), 2924 (w), 2847 (m), 1609 (vs), 1581 (s), 1539 (s). ^{1}H-NMR (ppm, in C_6D_6): 8.56 (s, 2H, $-CH=$N), 6.6–8.0 (m, 12H, Ar–*H*), − 0.3 (s, 3H, GaCH_3). MS: 400 (1.71%), 399 (6.85%), 398 (0.64%), 385 (68.26%), 384 (22.6%), 383 (100%), 316 (1.19%), 105 (3.64%), 84 (65.9%), 71 (18.6%), 69 (26.8%). Anal. Calc. for $C_{21}H_{17}N_2O_2Ga$: C, 63.20; H, 4.29; N, 7.02. Found: C, 63.10; H, 4.16; N, 7.01%.

*3.5. Synthesis of methyl-N,N′-bis(salicylidene)ethylenediaminogallium (**5**)*

Compound **5** was prepared in a manner similar to that described for **4** from trimethylgallium (0.23 g, 2 mmol) and *N*,*N*-ethylenebis(salicylideneimine) (0.536 g, 2 mmol) and was isolated as pale yellow solid. Yield: 0.59 g (85%); m.p. > 290°C (dec). IR (cm^{-1}): 3058 (w), 3022 (w), 2924 (w), 2917 (w), 2846 (w), 1630 (vs), 1581 (s), 1539 (s), 1461 (s), 1279 (s), 1025 (s), 913 (s), 744 (s). ^{1}H-NMR (ppm, in C_6D_6): 8.23 (s, 2H, $-CH=N$), 6.60–7.50 (m, 8H, Ar–*H*), 3.92 (m, 4H, $-N-CH_2CH_2-N-$), −0.26 (s, 3H, $GaCH_3$). MS: 351.7 (5.72%), 350.7 (32.72%), 336.7 (70.12%), 335.6 (20%), 334.7 (100%), 267.8 (15.89%), 70.8 (7.13%), 68.8 (12.09%). Anal. Calc. for $C_{17}H_{17}N_2O_2Ga$: C, 58.16; H, 4.88; N, 7.98. Found: C, 58.03; H, 4.84; N, 7.93%.

*3.6. Synthesis of diethyl-N,N′-bis(salicylidene)-1,2-phenylenediaminogallium (**6**)*

Compound **6** was prepared and purified in a manner similar to that described for **5** from 1,2-*N*,*N′*-phenylenebis(salicylideneimine) (0.632 g, 2 mmol) and triethylgallium (0.314 g, 2 mmol). Yield: 81.4%; m.p. 105°C. IR (cm^{-1}): 3454.6 (w), 3050 (w), 2933 (w), 2896 (m), 2861 (m), 1613 (vs), 1589 (m), 1570 (s), 1544 (s), 1468 (s), 1448 (s), 1388 (m), 1314 (m), 1276 (m), 1187 (w), 1151 (s), 1105 (w), 975 (w), 877 (w), 795 (w), 759 (s), 653 (w), 560 (w). ^{1}H-NMR (ppm, in C_6D_6): 12.76 (s, 1H, –*OH*), 8.47 (s, 1H, $-CH=N-Ga$), 7.97 (s, 1H, $-CH=N$), 6.67–7.27 (m, 12H, Ar–*H*), 1.10 (t, 6H, $GaCH_2CH_3$), 0.50 (q, 4H, $GaCH_2CH_3$). MS: 428.9 (5.46%), 385.0 (24.06%), 384.0 (8.61%), 382.9 (35.94%), 297.0 (3.26%), 296.0 (18.99%), 295.0 (4.16%), 294.0 (26.20%), 197.0 (9.96%), 196.0 (8.87%), 114.9 (36.91%), 104.0 (29.11%), 91.0 (14.98%), 78.0 (15.97%), 77.0 (86.82%), 70.9 (72.77%), 68.9 (100.0%). Anal. Calc. for $C_{24}H_{25}N_2O_2Ga$: C, 65.04; H, 5.69; N, 6.32. Found: C, 65.09; H, 5.79; N, 6.40%.

*3.7. Synthesis of diethyl-N,N′-bis(salicylidene)ethylenediaminogallium (**7**)*

Compound **7** was prepared in a manner similar to that described for **4** from *N*,*N′*-ethylenebis(salicylideneimine) (0.536 g, 2 mmol) and triethylgallium (0.32 g, 2.0 mmol) and was isolated as yellow crystals. Yield: 0.55 g (84.8%); m.p. 60°C. IR (cm^{-1}): 3495 (w), 3049 (w), 3018 (w), 2943 (m), 2899.5 (m), 2863 (s), 2807.8 (w), 1625.4 (vs), 1578.1 (s), 1541.5 (vs), 1497.8 (s), 1468.8 (s), 1447.3 (s), 1405 (s), 1372 (w), 1341 (m), 1315.6 (s), 1283.5 (m), 1248.1 (m), 1221.2 (m), 1197.4 (m), 1148.4 (s), 1043.2 (s), 1022 (m), 1003 (m), 859.5 (m), 758.4 (vs), 750.2 (vs), 649 (m), 607.8 (m), 562 (m). ^{1}H-NMR (ppm, in C_6D_6): 12.83 (s, 1H, –*OH*), 8.36 (s, 1H, $-CH=N-Ga$), 8.04 (s, 1H, $-CH=N$), 6.60–7.34 (m, 8H, Ar–*H*), 3.89 (s, 2H, $Ga-N-CH_3$), 3.78 (s, 2H, $-N-CH_3$), 1.14 (t, 6H, $Ga(CH_2CH_3)_2$), 0.43 (q, 4H, $Ga(CH_2CH_3)_2$). MS: 366.9 (15.94%), 364.9 (23.71%), 337.9 (12.37%), 336.9 (67.73%), 335.9 (19.63%), 334.9 (100%), 309.0 (4.42%), 307.9 (7.44%), 127 (2.2%), 107 (15.29%), 70.9 (34.4%), 68.9 (51.79%). Anal. Calc. for $C_{20}H_{25}N_2O_2Ga$: C, 60.79; H, 6.38; N, 7.09. Found: C, 60.74; H, 6.24; N, 7.08%.

Table 2
Crystal data, collection parameters, and refinements for $C_{21}H_{17}N_2O_2In$ (**1**)

Empirical formula	$C_{21}H_{17}N_2O_2In$
Formula weight	444.20
Space group	*P*212121 (no. 19)
Crystal system	Orthorhombic
a (Å)	9.718(2)
b (Å)	10.572(3)
c (Å)	17.604(3)
V (Å^3)	1808.6(7)
Z	4
Crystal dimensions (mm)	0.4 × 0.35 × 0.2
Crystal colour	Yellow
D_{calc} (g cm^{-3})	1.631
μ(Mo–K$_\alpha$) (cm^{-1})	13.02
Temperature (K)	296
T(max)/*T*(min)	1/0.7258
Diffractometer	Enraf–Nonius CAD-4
Monochromator	Graphite
Radiation	Mo–K$_\alpha$
$2\theta_{max}$ (°)	59.9
Index range (°)	$0 \le h \le 13$, $0 \le k \le 14$, $0 \le l \le 24$
Scan speed (° min^{-1})	8.24
Reflections collected	2994
Independent reflections observed $(I) > 3.00\ (\sigma(I))$	2791
No. variables	235
R(*F*)	0.038
wR	0.051
Goodness-of-fit	1.54
$\Delta\rho_{max}$ (e Å^{-3})	1.22
$\Delta\rho_{min}$ (e Å^{-3})	−1.22
$(\Delta/\sigma)_{max}$	0.0007

*3.8. Crystal structure determination of **1***

A suitable crystal of complex **1** was sealed in a thin-walled glass capilliary under a nitrogen atmosphere. Data collection was performed with Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD-4 diffractometer equipped with graphite monochromator. The structure was solved by the direct methods using MITHRIL [12] and subsequent Fourier techniques. Hydrogen atoms were added geometrically (before the final amendment). All calculations were performed using the TEXSAN [13] program system. ORTEPII [14] was used to produce the figures and CAD-4 software [15] was used for data collection and cell refinement. Crystallographic data are summarised in Table 2.

4. Supplementary material

Full information on the crystal structure can be ordered from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, upon request, quoting the deposition number CCDC-117964.

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[16] Symmetry code A: $-x$, $-0.5+x$, $1.5-z$; H(16)–C(5A) 3.18 Å, C(21)–C(5A) 3.953 Å.